

TOPOGRAPHICAL STUDY AND THERMAL STABILITY OF CONJUGATED POLYMER OF 1, 2-DICHLORO BENZENE AND NAPHTHALENE

SUDHA SHARMA¹ & B. TIWARI²

¹Research Scholar, Mewar University, Bari, Rajasthan, India

²Director, D.S. Institute of Technology and Management, Ghaziabad, Uttar Pradesh, India

ABSTRACT

Recently, tremendous progress has been made toward application of organic (small molecule/polymer) light-emitting diodes (OLEDs) in full colour flat panel displays and other devices. However, with current technologies, OLEDs are still struggling with high manufacturing costs which really limit the size of OLEDs panels and with life time, especially differential aging of colours. To be more cost-effective for fabricating OLEDs, we believe solution-processing would be an attractive path due to its simplicity and highly reduced equipment costs. This proceeding paper discusses our recent progress in development of new Co polymer (Poly-CIBN) having improved solubility and processibility

In the present work, we synthesized the Co-polymer of 1, 2 Di-Chloro Benzene with Naphthalene. The co-polymer (Poly-CIBN) have to be shifted in the PL spectra corresponding to the monomers. The property of the PPPs polymers like solubility, processibility gets quite improvised. The conjugated polymer so formed is analyzed on the basis of spectroscopic method of IR, NMR spectroscopy and AFM technique for topographical studies.

KEYWORDS: NMR, IR, AFM 1, 2 Di-Chloro Benzene, Naphthalene, Conjugated Polymer, PPPs, Topographical Study

INTRODUCTION

Conjugated polymers are organic macromolecules which consist at least of one backbone chain of alternating double- and single-bonds. Due to the fact that the p_z -orbitals of the carbon atoms which forms the π -orbitals of the alternating double-and single-bonds mesomerize more or less, i.e. the single and double bonds becomes similar, double-bonds overlaps also over the single bonds. Furthermore, the π -electrons can be easier moved from one bond to the other, what makes conjugated polymers to be one-dimensional semiconductors. Like inorganic semiconductors they can be doped, to increase their conductivity extremely. The most exciting development in the last decade was that of light emitting devices from polymers like polyphenylvinylene (PPV) and PPP.

Some of the frequently used conjugated polymers, in LED (Light Emitting Diode) are, poly (p – phenylene) (ppp) and poly (p – phenylene vinylene) (ppv).

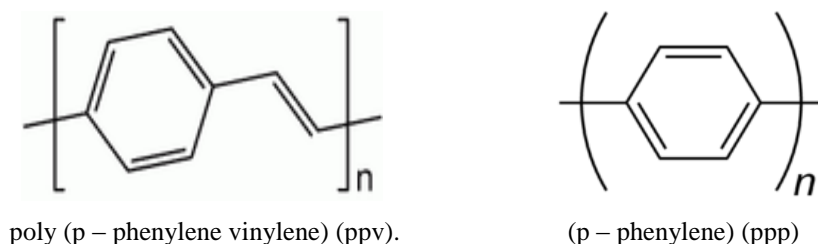


Figure 1

OLEDs promises superior performance in brightness and colour resolution, wider viewing angle, lower power consumption, a thin aspect ratio and better physical characteristics. The advantage makes OLED display attraction for the next generation mobile flat panel display (FPD). Polymer Light Emitting Diodes have a good chance to become the main display system in the near future since diodes have many advantage concerning preparation and operation over other display system.

THEORITICAL DETAILS

- **Naphthalene**

Molecular Structure - Naphthalene

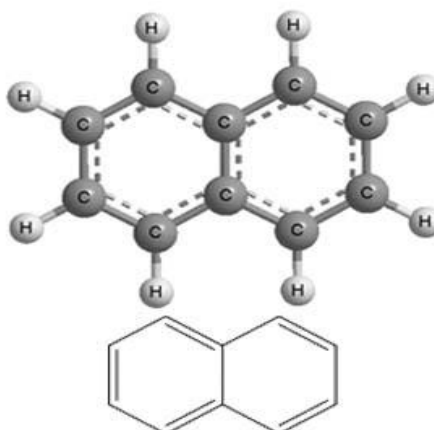


Figure 2

Table 1

Chemical Formula	C ₁₀ H ₈
Molecular Weight	128.16
Boiling Point	217.9 oC
Melting Point	80.2 oC
Flash Point	174 oF (open cup)
Vapor Density	4.42 (air = 1)
Density/Specific Gravity	1.162 at 20/4 oC
Vapor Pressure	0.082 mm Hg at 25 oC
Log Octanol/Water Partition Coefficient	3.3
Conversion Factor	1 ppm = 5.24 mg/m ³

The carbon–carbon bonds in naphthalene are not of the same length. The bonds C1–C2, C3–C4, C5–C6 and C7–C8 are about 1.36 Å (136 pm) in length, whereas the other carbon–carbon bonds are about 1.42 Å (142 pm) long. This difference, which was established by X-ray diffraction is consistent with the valence bond model of bonding in naphthalene that involves three resonance structures (as shown below); whereas the bonds C1–C2, C3–C4, C5–C6 and C7–C8 are double in *two* of the three structures, the others are double in only one.

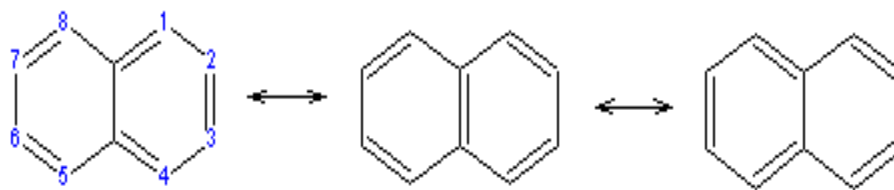


Figure 3

Like benzene, naphthalene can undergo electrophilic aromatic substitution.

- **1, 2 Di- Chloro Benzene**

Table 2: Physical Properties

Molecular Formula	C ₆ H ₄ Cl ₂
Molar mass	147.01 g/mol
Density	1.30 g/cm ³
Melting point	-17.03 °C, 256 K, 1 °F
Boiling point	180.5 °C, 454 K

Solubility: Soluble in most organic solvents

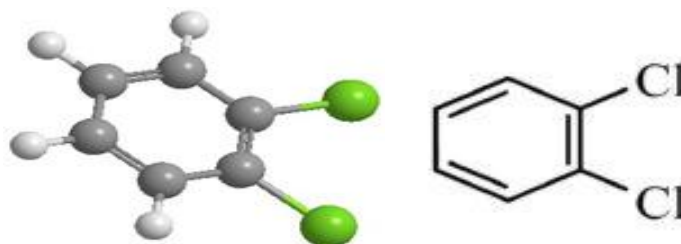


Figure 4

1, 2-Dichlorobenzene, or **orthodichlorobenzene** (ODCB), is an organic compound with the formula C₆H₄Cl₂. This colourless liquid is poorly soluble in water but miscible with most organic solvents. It is a derivative of benzene, consisting of two adjacent chlorine centres

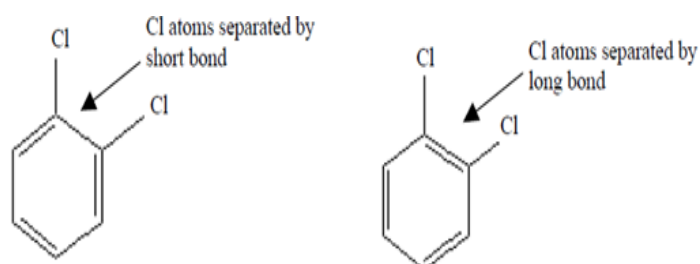


Figure 5

According to the structure proposed by Kekulé, there should be two isomers of 1,2-dichlorobenzene. In one structure, the chlorine atoms are separated by a single bond, and in the other, they are separated by a double bond. However, these isomers have never been isolated or detected.

AFM (Atomic Force Microscopy)

Atomic: AFM can achieve atomic resolution by using a sharp cantilever tip. Images obtained by AFM can distinguish two closely spaced atoms (but in reality it may not be always achievable).

Force: The image is created by quantifying the forces between the probe (cantilever tip) and the sample surface

Microscope: AFM amplifies the image of a sample.

AFM offers more power in characterizing the conducting polymer surfaces because it can precisely image the surface by maintaining a constant load force of the tip with respect to the substrate. However, its spatial resolution depends much on how sharp the tip is and the technique usually does not provide as sharp images as high-resolution SEM technique does. Thus, just as the SEM, the AFM did not distinguish spots of a chemically different nature, although AFMs currently available offer various ways of distinguishing the chemical functionalities.

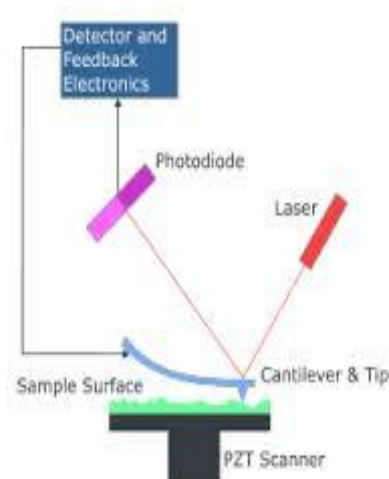


Figure 6

EXPERIMENTAL DATA

The synthesis of the co-polymer of naphthalene and 1,2 Di-chlorobenzene (poly-CIBN) has been carried out by the conventional Kovacic method using a FeCl_3 as catalyst. The heterogeneous reaction mixture consisting of the, catalyst, 1, 2 Dichlorobenzene and naphthalene is stirred for 4–6 hrs. at 35–40°C. After the completion of the reaction, the reaction mixture is washed with distilled water in order to remove the impurities. The orange brown polymer obtained is dried under vacuum. The characterization of the resultant polymer has been carried out by spectroscopic techniques.

Drying: The polymer was then dried at a temperature of about 40°C in a desiccator. After drying it became orange brown in colour.

Solubility: The polymer was insoluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, tetrahydrofuran (THF), Chlorobenzene, NMP, Xylene etc.

Characterization of Co-polymer of 1, 2Di-Chloro benzene and Naphthalene

FTIR Spectra of Copolymer of 1,2 Di-Chloro Benzene and Naphthalene

The sample of the polymer for FTIR was prepared in freshly cleaned dry K Br and the pellet of the sample was prepared by the hydraulic process. The FTIR spectrum was recorded. The peak at 3065 cm^{-1} was due C-H stretching of dichlorobenzene ring in polymer while the peaks at 2925 cm^{-1} and 2855 cm^{-1} was due to C-H stretching vibrations of naphthalene ring in the polymer. The band occurs in 1745 cm^{-1} aromatic region. The peaks at 1652 cm^{-1} and 1379 cm^{-1} were due to quadrant and semi-circle stretching vibrations of rings. The C-C in plane stretching of aromatic ring

present at 1164, 1093 cm^{-1} and 972 cm^{-1} . The peak at 720 cm^{-1} shows the Para substitution of the polymer. The C-H out of plane bending present at 582 cm^{-1}

Table 3

Promient Absorption Hand (CM^{-1})	Functional Group
3065(CM^{-1})	Sp ² C-H stretching (aromatic) 1,2 dichlorobenzene
2925-2855(CM^{-1})	C-H stretching stretch of naphthalene ring
1745(CM^{-1})	aromatic region
1632-1379(CM^{-1})	quadrant and semi-circle stretching vibrations of rings.
1164, 1093, 972(CM^{-1})	The C-C inplane stretching of aromatic ring
720(CM^{-1})	Para substitution of the polymer
582(CM^{-1})	C-H out of plane bending

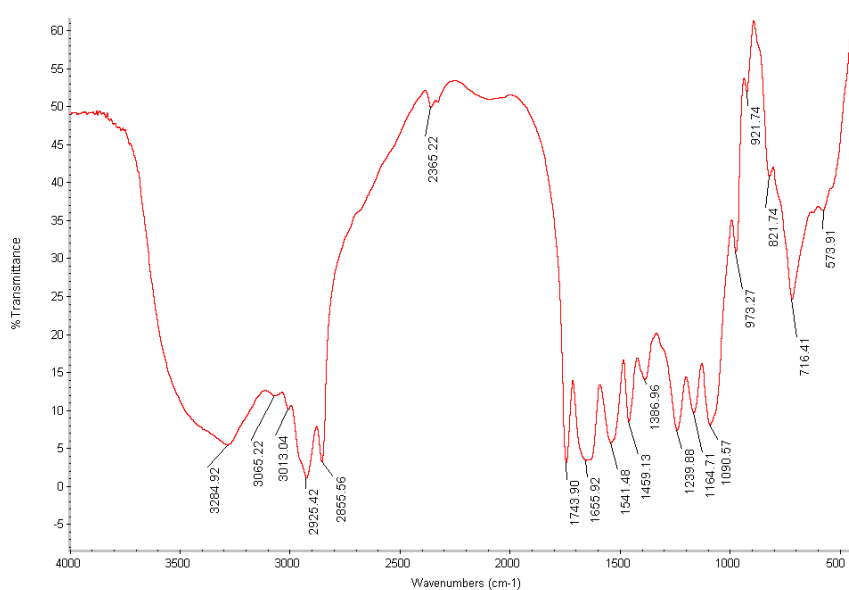


Figure 7

FTIR spectra of copolymer of 1,2 Di-chloro benzene and Naphthalene

NMR SPECTRA of THE COPOLYMER OF of 1,2 Di-Chloro Benzene and Naphthalene

Table 4

Types of Proton	Chemical Shift S(PPM) Conc of the Product: 1M (U)
Aromatic protons	7.885
Aromatic protons	7.411

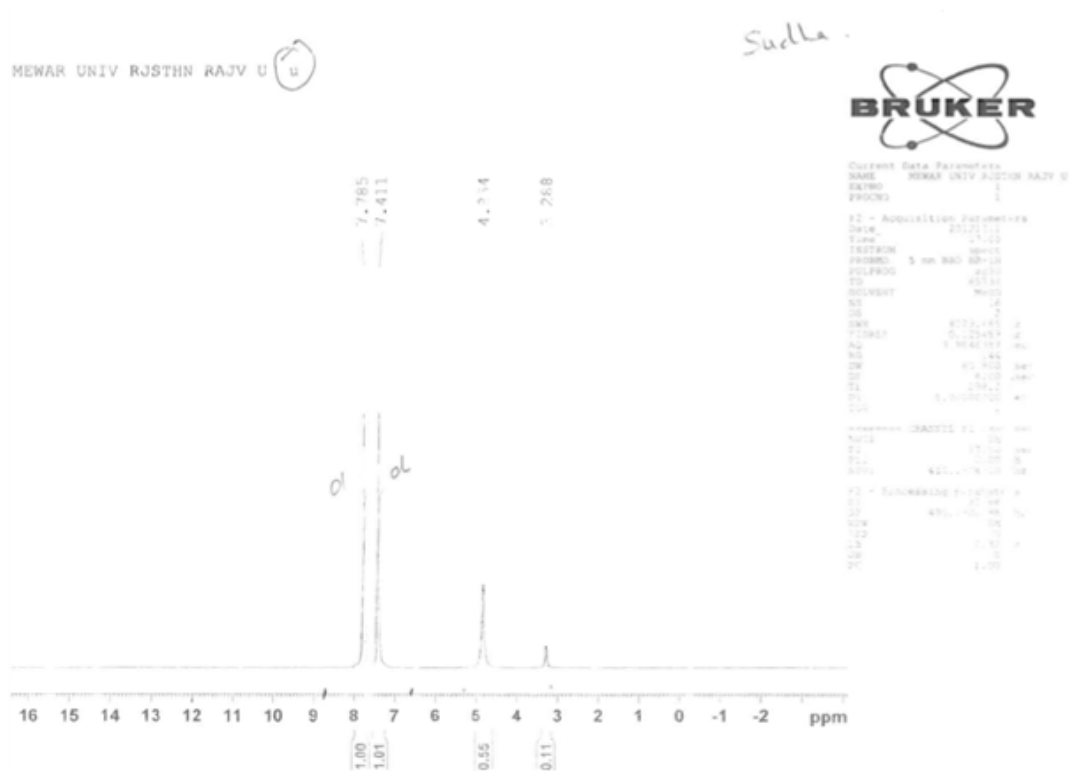


Figure 8

NMR SPECTRA of THE COPOLYMER OF 1, 2 Di-Chloro Benzene and Naphthalene

AFM Analysis

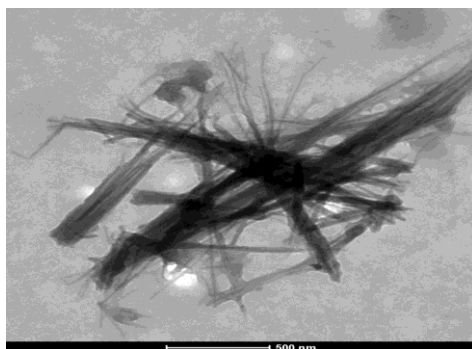


Figure 9



Figure 10

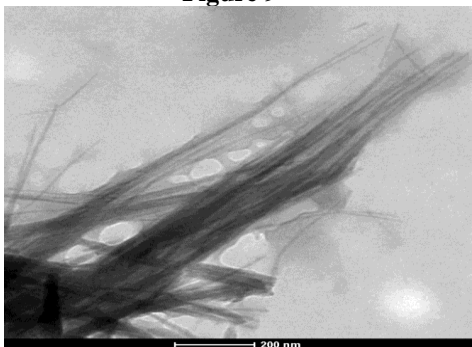


Figure 11

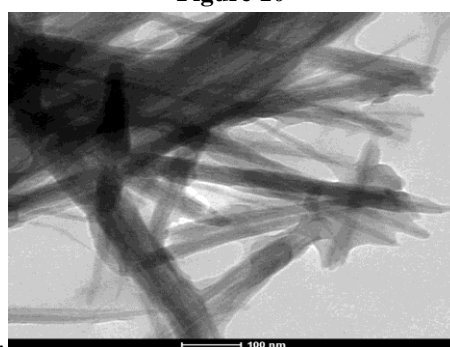


Figure 12

AFM Analysis

Observation of phase separated regions and of polymer crystals lying below smooth surface shows that not only topography but also elastic homogeneity can be observed in great detail with atomic force microscope.

RESULTS AND DISCUSSIONS

Co-polymer of 1,2 Dichlorobenzene and naphthalene has been prepared as a soluble poly-phenylene derivative. The polymer obtained is orange brown and soluble in organic solvents like chloroform, toluene and *N* methylpyrrolidone. The reaction can be represented as

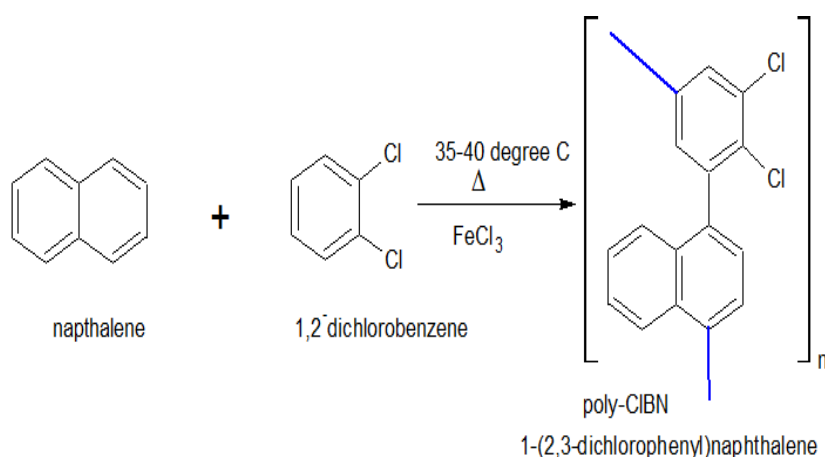


Figure 13

The (Poly-CIBN) conjugated polymer is synthesized and characterized by using various techniques such as UV, FTIR and NMR which are discussed as above.

CONCLUSIONS

We have synthesized a new co-polymer Incorporating 1, 2-Dichloro benzene and naphthalene using Kovacic technique, which has practical utility in the fabrication of OLEDs. The new polymer is soluble in common organic solvents and can be thermally evaporated to make thin films.. Therefore, the synthesized materials have good prospects for the industrial applications as electroluminescent materials in coming days.

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